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(54) Title: METHOD FOR FORMING A THREE-COMPONENT NITRIDE FILM CONTAINING METAL AND SILICON

(54) Titre: PROCÉDE POUR FORMER UN FILM DE NITRURE A TROIS COMPOSANTS CONTENANT DU METAL ET DU  
SILICIUM

## (57) Abstract

A method for forming a three-component film containing metal, silicon and nitrogen for use in semiconductor devices on a substrate. The method of the present invention comprises the steps of: preparing separate reactive gases each including at least one selected from the group consisting of a gaseous metal compound, a gaseous silicon compound and an ammonia gas under conditions such that the gaseous metal compound and the ammonia gas does not form a mixture; determining a sequential gas supply cycle of the reactive gases so that supplies of the gaseous metal compound, the gaseous silicon compound and the ammonia gas are each included at least once within one gas supply cycle; and applying the reactive gases to the substrate by repeating the gas supply cycle at least once. According to the present invention, a three-component nitride film can be formed with a uniform thickness despite unevenness of a semiconductor substrate surface.

## (57) Abrégé

L'invention concerne un procédé permettant de former un film à trois composants qui contient du métal, du silicium, et de l'azote, ce film étant destiné à être utilisé dans des dispositifs à semiconducteur placés sur un substrat. Le procédé de la présente invention consiste: à préparer des gaz réactifs séparés, chacun de ces gaz renfermant au moins un composé choisi dans le groupe constitué par un composé de métal gazeux, un composé de silicium gazeux, et un gaz ammoniacal, dans des conditions dans lesquelles ledit composé de métal gazeux et ledit gaz ammoniacal ne forment pas un mélange; à déterminer un cycle séquentiel d'alimentation de ces gaz réactifs de sorte que l'apport de chacun des composés de métal gazeux, de silicium gazeux, et de gaz ammoniacal s'effectue au moins lors d'un cycle d'alimentation; et enfin à appliquer ces gaz réactifs audit substrat, le cycle d'alimentation en gaz étant répété à une reprise au moins. Selon la présente invention, un film de nitrure à trois composants peut ainsi être formé, ce film présentant une épaisseur uniforme en dépit de l'aspect irrégulier de la surface du substrat à semiconducteur.

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| (54) Title: METHOD FOR FORMING A THREE-COMPONENT NITRIDE FILM CONTAINING METAL AND SILICON  |           |   |
| <p>(57) Abstract</p> <p>A method for forming a three-component film containing metal, silicon and nitrogen for use in semiconductor devices on a substrate. The method of the present invention comprises the steps of: preparing separate reactive gases each including at least one selected from the group consisting of a gaseous metal compound, a gaseous silicon compound and an ammonia gas under conditions such that the gaseous metal compound and the ammonia gas does not form a mixture, determining a sequential gas supply cycle of the reactive gases so that supplies of the gaseous metal compound, the gaseous silicon compound and the ammonia gas are each included at least once within one gas supply cycle, and applying the reactive gases to the substrate by repeating the gas supply cycle at least once. According to the present invention, a three-component nitride film can be formed with a uniform thickness despite unevenness of a semiconductor substrate surface.</p> <div data-bbox="609 1140 1307 1329"></div> <div data-bbox="690 1360 1209 1507"><p>a1 : Ar carrier gas bubbled in tetrakisdimethylamidotitanium</p><p>b1 : Ar gas</p><p>c1 : ammonia gas</p><p>d1 : silane gas</p></div> |           |   |

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**Description**

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**METHOD FOR FORMING A THREE-COMPONENT  
NITRIDE FILM CONTAINING METAL AND SILICON**

**TECHNICAL FIELD**

The present invention relates to a method for forming a film, and more particularly, to a method for forming a compound film of uniform thickness containing metal, silicon, and nitrogen for use in semiconductor devices on a substrate.

**BACKGROUND ART**

In the manufacture of semiconductor devices, a sputtered film of titanium nitride (TiN) is currently used as a diffusion barrier metal to prevent the diffusion of a metal interconnect into a silicon single crystal or an insulating layer. Additionally, the TiN is also used as a glue layer material to enhance adhesion when tungsten is used for forming an interconnect structure. However, a TiN film formed by sputtering or chemical deposition tends to have a columnar crystal structure, causing a problem that the metal interconnect material easily diffuses along its grain boundary. If a tungsten layer is formed on a TiN glue layer, the tungsten source gas  $WF_6$  also easily diffuses along the grain boundary of the TiN layer to cause damage to the TiN glue layer.

Such problems can be alleviated by using a nano-crystalline material with extremely small grains or an amorphous material as a diffusion barrier material. A three-component nitride containing silicon and a refractory metal such as titanium, tantalum or tungsten is promising for such material.

With the trend to continue to miniaturize semiconductor integrated circuits to achieve submicron feature sizes, the width of an interconnect line becomes smaller and the aspect ratio of a contact hole becomes higher. Sputtering method is inadequate to form a film of a uniform thickness on such a structure because the method has a certain directivity. Accordingly, it is required that a uniform film of about 10nm thickness is formed on a surface having holes of high-aspect ratio, that is, on an extremely uneven surface even using other deposition methods. Although chemical deposition is typically used to form a uniform thickness film, good step

5 coverage can not be obtained under a chemical deposition condition that deposition  
sources react violently in gas phases. Particularly in the case of using alkylamido  
10 metal compound to chemically deposit a metal nitride film, the deposited metal  
nitride film has a bad step coverage due to the reaction between gaseous alkylamido  
5 metal compound and ammonia gas.

15 Unlike conventional chemical deposition methods where thin film sources  
are simultaneously supplied on a substrate, the sequential deposition method where  
the sources are sequentially supplied on a substrate enables formation of a uniform  
thickness thin film because it can be formed only by chemical reaction of the  
20 substrate surface. This method is well described in the following book; T. Suntola and  
M. Simpson eds., *Atomic Layer Epitaxy*, Blackie, London, 1990. However, the  
applications of this method have been limited to the formation of a two component  
film or a composite oxide film containing more than three components.

#### 25 15 DISCLOSURE OF INVENTION

Accordingly, it is an object of the present invention to provide a method for  
forming a three-component nitride film containing metal and silicon for use in a  
30 barrier layer which effectively prevents the diffusion of metal interconnects of  
semiconductor devices.

20 Another object of the present invention is to provide a process by which a  
three-component nitride film containing metal and silicon is formed with a uniform  
35 thickness despite unevenness of a semiconductor substrate surface.

In order to accomplish the aforementioned object, the present invention  
provides a method for forming a three-component nitride film containing metal and  
40 25 silicon on a substrate, the method comprising the steps of: (a) preparing separate  
reactive gases each including at least one selected from the group consisting of a  
gaseous metal compound, a gaseous silicon compound and an ammonia gas under  
conditions such that the gaseous metal compound and the ammonia gas does not form  
45 a mixture; (b) determining a sequential gas supply cycle of the reactive gases so that  
supplies of the gaseous metal compound, the gaseous silicon compound and the  
30 ammonia gas are each included at least once within one gas supply cycle; and (c)  
applying the reactive gases to the substrate by repeating the gas supply cycle at least  
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5  
once.

10 The reactive gases include only five types of gases such as a gaseous metal compound, a gaseous silicon compound, an ammonia gas, a mixture of a gaseous metal compound and a gaseous silicon compound, a mixture of a gaseous silicon  
5 compound and an ammonia gas because gaseous metal compound and the ammonia gas react each other thus should not form a mixture.

### 15 BRIEF DESCRIPTION OF DRAWINGS

FIGS. 1A to 1C are graphs showing the gas supply cycles regardless of  
10 absolute magnitude in flow rate and deposition time according to the embodiments of the present invention.

### BEST MODE FOR CARRYING OUT THE INVENTION

25 In the embodiment of the present invention, various gas supply cycles can be determined as follows.

15 First, between the supplies of the reactive gases, supplies of a gas not reacting with any of the reactive gases are inserted. The respective reactive gas supplies of a gaseous metal compound, a gaseous silicon compound and an ammonia gas are preferably arranged in a cyclic permutation order, and supplies of a gas not  
30 reacting any of the three component gases are inserted therebetween. For example, the supply cycle may be determined to be "gaseous metal compound→non-reacting gas→gaseous silicon compound→non-reacting gas→ammonia gas→non-reacting  
35 gas" or "gaseous metal compound→non-reacting gas→ammonia gas→non-reacting gas→gaseous silicon compound→non-reacting gas", respectively. In the chemical  
40 deposition, such a supply cycle is repeated to form a film of desired thickness.

25 Second, because the reactive gases include gas mixtures, the respective supplies of reactive gases containing a gaseous metal compound and an ammonia gas are arranged within the supply cycle and supplies of a gas not reacting with any of the  
45 two reactive gases are inserted therebetween. Here, the reactive gas containing a metal compound may be a sole gaseous metal compound or a mixture of a gaseous  
30 metal compound and a gaseous silicon compound. Additionally, the same may be a reactive gas containing an ammonia gas. In this case, the supply cycle may be  
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5 determined, for example, to be "mixture of a gaseous metal compound and a gaseous  
silicon compound→non-reacting gas→ammonia gas→non-reacting gas", "gaseous  
10 metal compound→non-reacting gas→mixture of an ammonia gas and a gaseous  
silicon compound→non-reacting gas", or "mixture of a gaseous metal compound and  
5 a gaseous silicon compound→non-reacting gas→mixture of an ammonia gas and a  
gaseous silicon compound→non-reacting gas", respectively. In the above methods of  
15 determining supply cycle, the non-reacting gas is supplied to prevent the reaction of  
reactive gases.

Third, a gaseous silicon compound, instead of a non-reacting gas, may be  
10 used to prevent the vapor reaction between a gaseous metal compound and an  
ammonia gas. Accordingly, the supply cycle is determined by inserting a gaseous  
silicon compound between the respective supplies of the reactive gases containing a  
metal compound and ammonia. For example, the respective reactive gas supplies of a  
25 gaseous metal compound, a gaseous silicon compound and an ammonia gas are  
15 arranged in a cyclic permutation order, and supplies of a gaseous silicon compound  
are inserted therebetween. That is, the supply cycle may be "gaseous metal  
compound→gaseous silicon compound→ammonia gas→gaseous silicon compound".  
30 Instead of the above supply cycle, the supply cycle may be "mixture of a gaseous  
metal compound and a gaseous silicon compound→gaseous silicon  
20 compound→ammonia gas→gaseous silicon compound", "gaseous metal  
35 compound→gaseous silicon compound→mixture of an ammonia gas and a gaseous  
silicon compound→gaseous silicon compound", or "mixture of a gaseous metal  
compound and a gaseous silicon compound→gaseous silicon compound→mixture of  
40 an ammonia gas and a gaseous silicon compound→gaseous silicon compound". As  
25 described above, the supplies of reactive gases, such as a gaseous silicon compound,  
not reacting with other reactive gases can be inserted between the supplies of other  
reactive gases to prevent vapor phase reactions.

45 Fourth, the supply cycles can be differently determined to control the  
stoichiometric composition of a film during the deposition. The desired control of  
30 stoichiometric composition provides better matches of physical properties between  
the deposited film and the upper/lower layers thereof. Such physical properties  
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5 include a contact resistance, a step coverage, etc. For example, in the case of depositing a three-component nitride film containing titanium and silicon on a silicon-rich underlayer, a silicon-rich film ( $\text{Ti}_x\text{Si}_y\text{N}$ ,  $x < y$ ) is deposited in the early stage of deposition to provide low contact resistance and then a titanium-rich film  
10 ( $\text{Ti}_x\text{Si}_y\text{N}$ ,  $x > y$ ) is deposited in the late stage of deposition to reduce the film resistance itself.

15 In order to form such a film, the supply cycle is determined to include supplies of gaseous silicon compound more than those of gaseous metal compound in the early stage of deposition whereas it is determined to include supplies of gaseous metal compound more than those of gaseous silicon compound in the late stage of  
20 deposition. For example, the supply cycle is determined to be "Si-N-Si-N-Ti-N-" in the early stage of deposition, "Si-N-Ti-N-" in the middle stage of deposition, "Si-N-Ti-N-Ti-N-" in the late stage of deposition, wherein Si is a gaseous silicon compound, N is an ammonia gas, and Ti is a gaseous titanium compound. In the above supply  
25 cycle, notation of non-reacting gas, which is supplied between the supplies of reactive gases, was omitted.

30 In some cases, the supply cycle may be "Si-N-Ti-N-Ti-N-Ti-N-Ti-N-Ti-N-" to lower the overall content of silicon in a deposited film while maintaining constant composition of silicon. In the embodiments, the metal included in the metal  
35 compound is preferably a refractory metal, and more preferably, the refractory metal is titanium, tantalum, or tungsten. Additionally, the metal compound may be an organometallic compound or a halogenated metallic compound. In the case of using an organometallic compound, it is preferably an amido or imido compound of a metal. More preferably, the amido compound of a metal is an amidotitanium compound and  
40 most preferably the amidotitanium compound is tetrakisdimethylamidotitanium or tetrakisdietihamidotitanium.

45 Likewise, for example, if tantalum tris-diethylamido-t-butylimide is used as a metal source, a three-component nitride film containing tantalum and silicon can be obtained.

50 The silicon compound is preferably a compound comprised of hydrogen and silicon, which is represented by  $\text{Si}_n\text{H}_{2n+2}$ , wherein n is a natural number of not more than 5. Preferably, the non-reacting gas is  $\text{H}_2$ , He,  $\text{N}_2$ , or Ar.

5 In the chemical deposition step, the temperature of the substrate is preferably maintained lower than the thermal decomposition temperature of the metal compound to prevent the formation of a film with poor step coverage due to vapor phase  
10 reaction.

5 The present invention will be further described in the following examples and will be compared with other examples, but the present invention should not be construed as being limited thereto.  
15

All the reactions were carried out in a reactor made of stainless steel. The pressure in the reactor during the deposition was 1 Torr, while the temperature of a  
10 silicon substrate contained in the reactor was maintained at 180°C. Tetrakisdimethylamidotitanium, a metallic source, was fed to the reactor by bubbling an argon carrier gas at a temperature of 25°C. The temperature of gas supply line was maintained at 100°C to prevent the condensation of the metallic source.  
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25 [example 1]

The cycle was comprised of sequential supplies of an argon carrier gas bubbled in tetrakisdimethylamidotitanium at a flow rate of 100 sccm for 5 seconds, an  
30 argon gas at a flow rate of 100sccm for 10 seconds, an ammonia gas at a flow rate of 143 sccm for 5 seconds, an argon gas at a flow rate of 100 sccm for 10 seconds, a  
20 silane ( $\text{SiH}_4$ ) gas at a flow rate of 38sccm for 5 seconds, and an argon gas at a flow rate of 100 sccm for 10 seconds. The cycle was repeated by 200 times, as shown in FIG. 1A. Auger spectrum analysis of the deposited film indicated compositions of titanium, nitrogen, silicon, carbon, and oxygen with their specific peaks.  
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40 [example 2]

The cycle was comprised of sequential supplies of an argon carrier gas bubbled in tetrakisdimethylamidotitanium at a flow rate of 91 sccm mixed with a  
45 silane gas at a flow rate of 9sccm for 5 seconds, an ammonia gas at a flow rate of 143 sccm for 5 seconds, and an argon gas at a flow rate of 100 sccm for 10 seconds. The  
30 cycle was repeated by 200 times, as shown in FIG. 1B. Auger spectrum analysis of the deposited film indicated compositions of titanium, nitrogen, silicon, carbon, and oxygen with their specific peaks.  
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## [example 3]

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The cycle was comprised of sequential supplies of an argon carrier gas bubbled in tetrakisdimethylamidotitanium at a flow rate of 100 sccm for 5 seconds, an argon gas at a flow rate of 100 sccm for 10 seconds, an ammonia gas at a flow rate of 13 sccm mixed with a silane gas at a flow rate of 38 sccm for 5 seconds, and an argon gas at a flow rate of 100 sccm for 10 seconds. The cycle was repeated by 200 times, as shown in FIG. 1C. Auger spectrum analysis of the deposited film indicated compositions of titanium, nitrogen, silicon, carbon, and oxygen with their specific peaks.

## [comparative example 1]

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The cycle was comprised of sequential supplies of an argon carrier gas bubbled in tetrakisdimethylamidotitanium at a flow rate of 100 sccm for 5 seconds, an argon gas at a flow rate of 100 sccm for 10 seconds, a silane gas at a flow rate of 38 sccm for 5 seconds, and an argon gas at a flow rate of 100 sccm for 10 seconds. The cycle was repeated by 200 times, and no film, however, was formed on the silicon substrate.

## 20 [comparative example 2]

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The cycle was comprised of sequential supplies of an ammonia gas at a flow rate of 143 sccm for 5 seconds, an argon gas at a flow rate of 100 sccm for 10 seconds, a silane gas at a flow rate of 38 sccm for 5 seconds, and an argon gas at a flow rate of 100 sccm for 10 seconds. The cycle was repeated by 200 times, and no film, however, was formed on the silicon substrate.

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The comparative examples show that reactive gases of a gaseous metal compound, a gaseous silicon compound and an ammonia gas each should be included at least once within the gas supply cycle to form a three-component nitride film containing metal and silicon.

## Claims

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## WHAT IS CLAIMED IS :

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1. A method for forming a three-component nitride film containing metal and silicon on a substrate, said method comprising the steps of:

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5 (a) preparing separate reactive gases each including at least one selected from the group consisting of a gaseous metal compound, a gaseous silicon compound and an ammonia gas under conditions such that the gaseous metal compound and the ammonia gas do not form a mixture;

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10 (b) determining a sequential gas supply cycle of said reactive gases so that supplies of said gaseous metal compound, said gaseous silicon compound and said ammonia gas are each included at least once within one gas supply cycle; and

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(c) applying said reactive gases to said substrate by repeating said gas supply cycle at least once.

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15 2. The method of claim 1, wherein said one gas supply cycle comprises supplies of a gas not reacting with any of said reactive gases, each supply being inserted between the supplies of said reactive gases.

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3. The method of claim 2, wherein the respective supply cycles are determined to include different times of reactive gas supplies to change the stoichiometric composition of said three-component nitride film, providing better matches of physical properties between said three-component nitride film and the upper/lower layers thereof.

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25 4. The method of claim 3, wherein said chemical vapor deposition step is conducted by repeating supply cycles, said supply cycles each including relatively more gaseous silicon compound supplies in the early stage of said deposition step while said supply cycles each including relatively more gaseous metal compound supplies in the late stage of said deposition step, to reduce the contact resistance between said three-component nitride film and the upper/lower layers thereof.

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5. The method of claim 2, wherein, within said one supply cycle, the respective

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supplies of a gaseous metal compound, a gaseous silicon compound and an ammonia gas are arranged in a cyclic permutation order, supplies of a gas not reacting any of the three component gases being inserted between said reactive gas supplies.

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- 5 6. The method of claim 1, wherein, within said one supply cycle, the respective supplies of reactive gases containing a gaseous metal compound and an ammonia gas are arranged, supplies of a gas not reacting with any of said two reactive gases being inserted therebetween.

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- 10 7. The method of claim 1, wherein, within said one supply cycle, the respective supplies of reactive gases containing a gaseous metal compound and an ammonia gas are arranged, supplies of a gaseous silicon compound being inserted therebetween.

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- 25 8. The method of claim 1, wherein, within said one supply cycle, the respective supplies of a gaseous metal compound, a gaseous silicon compound and an ammonia gas are arranged in a cyclic permutation order, supplies of a gaseous silicon compound being inserted therebetween.

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9. The method of claim 1, wherein said metal is selected from the refractory metal group consisting of titanium, tantalum and tungsten.

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10. The method of claim 1, wherein said metal compound is an organometallic compound.

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- 25 11. The method of claim 1, wherein said metal compound is a halogenated metallic compound.

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12. The method of claim 10, wherein said organometallic compound includes at least one amido or imido group.

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13. The method of claim 12, wherein said amido-metallic compound is an amido-titanium compound.

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14. The method of claim 13, wherein said amido-titanium compound is tetrakisdimethylamidotitanium or tetrakisdialkylamidotitanium..

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5 15. The method of claim 12, wherein said organometallic compound is tantalum tris-diethylamido-t-butylimide.

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16. The method of claim 1, wherein said silicon compound is a compound comprised of hydrogen and silicon, which is represented by  $\text{Si}_n\text{H}_{2n-2}$ , wherein n is a natural number of not more than 5.

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17. The method of claim 2, wherein said non-reacting gas is selected from the group consisting of  $\text{H}_2$ , He,  $\text{N}_2$ , and Ar.

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15 18. The method of claim 1, wherein the temperature of said substrate is maintained lower than the thermal decomposition temperature of said metal compound during chemical deposition.

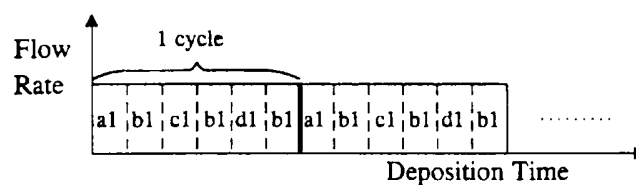
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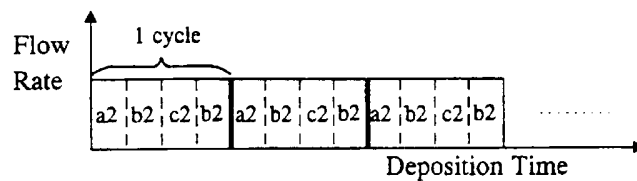
**FIG. 1A**

a1 : Ar carrier gas bubbled in tetrakisdimethylamidotitanium

b1 : Ar gas

c1 : ammonia gas

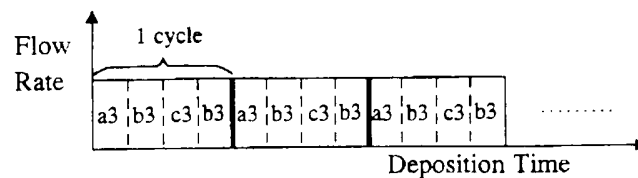
d1 : silane gas

**FIG. 1B**

a2 : Ar carrier gas bubbled in tetrakisdimethylamidotitanium  
mixed with silane gas

b2 : Ar gas

c2 : ammonia gas

**FIG. 1C**

a3 : Ar carrier gas bubbled in tetrakisdimethylamidotitanium

b3 : Ar gas

c3 : mixture of ammonia gas and silane gas